

## MODELING BIPHASIC SORPTION AND DESORPTION OF HYDROPHOBIC ORGANIC CONTAMINANTS IN SEDIMENTS

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**Abstract**—A model was developed to predict biphasic sorption and desorption of hydrophobic organic compounds in contaminated sediments. The model was based on relatively rapid porous diffusion in amorphous organic carbon and slow solid-phase diffusion in condensed-phase organic carbon. The model was used to simulate measured solid–fluid phase desorption (rates and pore-water concentrations) for four polycyclic aromatic hydrocarbons exhibiting a range of hydrophobicities (phenanthrene, anthracene, pyrene, and benzo[a]pyrene) in two field-contaminated sediments from Utica Harbor (Utica, NY, USA) and Rouge River (Detroit, MI, USA). Pore-water concentrations have been related to bioavailability, indicating the potential usefulness of the model to predict bioavailability. Key model parameters included the fraction of condensed-phase carbon (estimated by combustion at 375°C), partition coefficient to the condensed-phase carbon (estimated by desorption measurements on coal-like particles physically separated from Utica Harbor sediments), and diffusivity and ratio of volume to surface area of the condensed-phase organic matter (fitted to measured desorption data on both sediments and for the measured polycyclic aromatic hydrocarbons). Best fit for the diffusion coefficient in the condensed-phase organic matter was  $8.5 \times 10^{-20}$  m<sup>2</sup>/s, and ratio of volume to surface area was 2  $\mu$ m. These parameters estimated measured pore-water concentrations of all polycyclic aromatic hydrocarbons in both sediments with an average error of 46% and a correlation coefficient of 0.76 and the fast-desorbing fractions (as measured by the fraction removed with a nonpolar polymeric sorbent XAD-2) with an average error of approximately 30% and a correlation coefficient of 0.54 (14% and 0.76, respectively, for all but benzo[a]pyrene). Modeling results were relatively insensitive to the two fitted parameters, with changes of an order of magnitude or more being required to affect the correlation between the model and observations significantly.

**Keywords**—Hydrophobic organic contaminants   Modeling   Sediments   Sorption   Condensed-phase organic carbon

## INTRODUCTION

Recent research has revealed that the availability of sediment-associated hydrophobic organic contaminants is critical in defining exposure, uptake, or risk of contaminants to receptor organisms in the environment. Measured pore-water concentrations have been found to reflect availability and uptake in organisms better than total sediment concentrations do (see, e.g., [1–3]). The identification of that portion of the contaminant that can partition into the mobile fluid phases also is the basis for indirect measures of availability (e.g., the use of supercritical CO<sub>2</sub> [4], the use of strong solid sorbents [5], and the use of biological extractants [6]). The ability of physicochemical partitioning measurements to indicate or control bioavailability suggests that physicochemical models of contaminant desorption could prove to be useful in predicting bioavailability. It is toward the development of such a model that the present study is directed.

In evaluating contaminant fate, risk, and endpoints for remediation, the total solid-phase concentration often has been used and linear partitioning assumed [7]. Because most hydrophobic organic contaminants are believed to reside in soil/sediment organic matter in natural sorbents [8,9], the organic carbon-normalized sediment–water partition coefficient ( $K_{oc}$ ) frequently is used to characterize sorption capacity. This linear and reversible partitioning model [7] suggests that all the sediment-associated contaminant is available to partition into the

mobile phase. Evidence is increasing, however, that a fraction of the sediment-bound contaminant is not easily desorbed, which results in reduced availability of the desorption-resistant fraction of contaminant [1,10–14]. Empirical biphasic models [15,16] have been proposed to describe the desorption phenomenon, which includes a rapid release of a reversible labile fraction followed by a slow release of the resistant fraction. These empirical kinetic models are not mechanistic, however, and have little predictive capability.

Other models, both conceptual and mathematical, are mechanistic in nature. Desorption resistance has been ascribed to the heterogeneity of organic matter in sediments. Much of the natural organic matter in near-surface sediments is relatively amorphous, diagenetically young material, and this material typically exhibits rapid sorption and desorption as well as an equilibrium that is well-characterized by the organic carbon-normalized partition coefficient. Condensed-phase carbon, which may have anthropogenic as well as natural sources and which has been referred to as hard carbon, soot, black carbon, glassy polymer, coal-derived, and so on, has been widely found in field-contaminated sediments and has been postulated to be responsible for the desorption resistance of contaminants in sediments [17–24]. The condensed-phase carbon has been aged diagenetically by either slow natural processes or relatively rapid combustion or pyrolysis reactions [25]. The condensed-phase organic carbon exhibits extremely high sorption capacity, as indicated by an elevated partition coefficient [14,26], and it is highly reduced and condensed in form so that the

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diffusion rate of contaminant in this phase is extremely slow [20]. Various models have been proposed that recognize the differences between the amorphous and condensed-phase organic carbon, such as the distributed reactivity model [17], the dual mode model [22], and biphasic models [19,21]. These models have been used to explain observed sorption/desorption behavior and apparent partition coefficients between the solid phase and the adjacent pore water. These models have not been designed, however, to predict the kinetics of desorption or apparent partition coefficients without extensive sediment and contaminant-specific sorption and desorption measurements. It would be useful to be able to predict pore-water concentrations or the kinetics of desorption on the basis of a model with parameters that are readily available or that can be estimated from readily available measurements.

Because the condensed-phase carbon is relatively refractory and not easily separated by size or density separations, the fraction of organic carbon remaining after sediment combustion at 375°C may be a reasonable indication of the fraction of condensed-phase carbon [19]. Chai et al. [27] characterized the relationship between the desorption-resistant phenomena and the condensed-phase organic carbon content for four polycyclic aromatic hydrocarbon (PAH)-contaminated sediments (two laboratory-inoculated and two field-contaminated sediments). No strong correlation between desorption resistance and condensed-phase organic carbon contents for the two laboratory-inoculated sediments were observed, apparently because of the relatively short duration of the experiment and the limited contribution of condensed-phase carbon to partitioning over such a short time. A strong correlation between condensed-phase carbon and desorption resistance was observed, however, for field-contaminated sediments. A model is sought that can use this measure of the quantity of condensed-phase carbon (combustion at 375°C, as described by Gustafsson et al. [19]) that can predict desorption and apparent partition coefficients in field sediments as a potential indicator of bioavailability [1–3]. A critical parameter that characterizes both desorption and the apparent partition coefficient is the fraction of contaminants that are desorbed rapidly. This model was evaluated with data from the two field-contaminated sediments from the Utica Harbor (Utica, NY, USA) and the Rouge River (Detroit, MI, USA). Chai et al. [27] measured the fast-release fraction for these sediments by short-term exposure to a strong sorbent, the nonpolar polymeric resin XAD-2. Chai et al. [27] also related the apparent partition coefficient and the desorption kinetics of the bulk sediments to the fast-release fraction as measured in this manner. Thus, a major goal of the proposed model is to predict the fast-release fraction of particular contaminants from sediments.

## MATERIALS AND METHODS

### *Development of the model*

The partitioning behavior of contaminants in sediment represents the balance between the kinetics and capacity of various organic carbon matrices in sediment. The slow kinetics of the desorption-resistant fraction of contaminants is assumed to be attributable to the slow (effectively solid-phase) diffusion of contaminants in the condensed-phase organic carbon and limited exposed surface area. Conversely, fast kinetics is assumed to be associated with sorption and desorption onto the amorphous organic matter. The rate of sorption or desorption from amorphous organic matter was assumed to be intra-aggregate diffusion through the porous structure of sediment re-

tarded by sorption onto adjacent solid surfaces. Contaminant in any intraparticle pore water is assumed to be in local equilibrium with contaminant sorbed at the interface of the solid phase ( $K_{OC}$ ). The  $K_{OC}$  applicable to exposed amorphous surfaces was assumed to be given by literature estimates (described below) and related to the hydrophobicity of the contaminant. The  $K_{OC}$  applicable to exposed condensed-phase carbon was measured [27]. In both cases, only the interface, not the entire solid phase, was assumed to be in equilibrium with the pore water.

For simplicity, diffusion is assumed to be one-dimensional, although evaluations with the completed model showed that the results are essentially independent of assumed geometry. The assumption of one-dimensional diffusion is effectively identical to the assumption that organic matter is a slab with a length scale normal to the exposed surface as defined by the ratio of volume to surface area ( $V/A$ ). The ratio of volume to surface area appears implicitly in the equations given below, in that it defines the scaling of the distance coordinate,  $x$ .

Subject to these assumptions, the concentration of contaminant in the amorphous organic matter is governed by

$$\frac{\partial C_t^A}{\partial t} = D_{\text{eff}}^A \frac{\partial^2 C_W^A}{\partial x^2} \quad (1)$$

where  $C_W^A$  is the contaminant concentration in the pore water of the amorphous organic matter (mg/L);  $t$  is time;  $D_{\text{eff}}^A$  is the effective diffusivity of contaminant in the amorphous organic matter ( $\text{m}^2/\text{s}$ );  $C_t^A$  is the total contaminant concentration in the amorphous organic matter, including both contaminant in pore water and in solid phase (mg/L); and

$$C_t^A = C_W^A(\varepsilon + \rho^A \cdot K_{OC}^A \cdot f_{OC/OM}^A) \quad (2)$$

$$D_{\text{eff}}^A = D \cdot \varepsilon^{4/3} \quad (3)$$

where  $D$  is the diffusivity of contaminant in water ( $\text{m}^2/\text{s}$ ),  $\varepsilon$  is the porosity of the amorphous organic matter,  $\rho^A$  is the bulk density of the amorphous organic matter ( $\text{kg}/\text{L}$ ),  $f_{OC/OM}^A$  is the fraction of organic carbon to the amorphous organic matter, and  $K_{OC}^A$  is the organic carbon-normalized partition coefficient of contaminant in the amorphous organic matter. Note that the model describes diffusion in the organic matter, not in the bulk sediment particle or just the organic carbon fraction, hence the need for the fraction organic carbon within the organic matter fraction. Substituting Equation 2 into Equation 1 gives

$$\frac{\partial C_W^A}{\partial t} = \frac{D_{\text{eff}}^A}{R_f^A} \cdot \frac{\partial^2 C_W^A}{\partial x^2} \quad (4)$$

where  $R_f^A$  is the retardation factor in the amorphous organic matter and

$$R_f^A = \varepsilon + \rho^A \cdot K_{OC}^A \cdot f_{OC/OM}^A \quad (5)$$

The corresponding equation governing the concentration in the condensed-phase organic matter is

$$\frac{\partial C_S^C}{\partial t} = D^C \frac{\partial^2 C_S^C}{\partial x^2} \quad (6)$$

where  $C_S^C$  is the contaminant concentration in the condensed-phase organic matter (mg/kg) and  $D^C$  is the diffusivity of contaminant in the condensed-phase organic matter ( $\text{m}^2/\text{s}$ ). If we define a virtual contaminant concentration ( $C_W^C$ ) in the condensed-phase organic matter that is the hypothetical pore-water concentration that would be in equilibrium with the condensed-

phase carbon, allowing it to be compared directly to the pore-water concentration in the amorphous organic matter, then

$$C_W^C = \frac{C_S^C}{K_P^C} = \frac{C_S^C}{K_{OC}^C \cdot f_{oc/om}^C} \quad (7)$$

Equation 6 can be rewritten as

$$\frac{\partial C_W^C}{\partial t} = D^C \frac{\partial^2 C_W^C}{\partial x^2} \quad (8)$$

where  $f_{oc/om}^C$  is the organic carbon content of the condensed-phase organic matter and  $K_{OC}^C$  is the organic carbon-normalized partition coefficient of contaminant in the condensed-phase organic matter.

Equations 1 and 8 were solved for  $C_W^A(x, t)$  and  $C_W^C(x, t)$  given different boundary conditions and initial conditions (refer to details below) for sorption and desorption processes and to evaluate effective partition coefficients. The process of “aging,” during which observations have noted an increasing influence of desorption resistance with time, also was simulated with the model. For the two field-contaminated sediments, the predicted desorption rates and apparent sediment–water partitioning were compared to measurements. For purposes of the latter calculations, the initial contaminant concentration distribution in the field-contaminated sediments was simulated by sorption during long exposure (50 years) to a constant concentration. The model partial differential equations with corresponding boundary conditions and initial conditions were solved by simultaneously using the finite element method and were implemented with a MatLab program. During simulations of sorption, the pore-water concentration is maintained constant, and the solid concentration initially is zero. Boundary conditions and initial condition for sorption are as follows.

Boundary conditions for amorphous organic matter and condensed-phase organic matter are

$$\begin{aligned} \frac{\partial C_W^{A \text{ or } C}}{\partial x} &= 0 \quad \text{at } x = 0 \\ C_W^{A \text{ or } C} &= C_{W0} \quad \text{at } x = \pm(V/A) \end{aligned} \quad (9)$$

where  $C_{W0}$  is the concentration of contaminant in the aqueous phase (nonzero during sorption simulations). Initial conditions during sorption simulations were  $C_W^A = 0$  and  $C_W^C = 0$ .

During desorption, the concentration in sediment pore water was assumed to be essentially zero:

$$\begin{aligned} \frac{\partial C_W^{A \text{ or } C}}{\partial x} &= 0 \quad \text{at } x = 0 \\ C_W^{A \text{ or } C} &= 0 \quad \text{at } x = \pm(V/A) \end{aligned} \quad (10)$$

Initial concentration profiles of intraparticle pore-water concentration in the amorphous organic matter ( $C_W^A$ ) and the virtual equivalent pore-water concentration in the condensed-phase organic matter ( $C_W^C$ ) during desorption simulations were defined by the concentration at the end of the sorption phase. These simulations could be used to predict the fraction of contaminant that could be removed by mixing the sediment with a strong sorbent, such as XAD-2 or Tenax [27]. This fraction is often used as a measure of the fast-desorbing fraction, and the remainder as an indication of the slow-desorbing fraction, of contaminants.

The model also was used to predict an apparent partition coefficient and desorption isotherms. Sorption onto and desorption from the condensed-phase carbon is sufficiently slow that apparent partition coefficients are essentially independent

of time except during sorption of very long duration (years to decades). The desorption isotherm was established by simulation of sediments with different initial contaminant concentrations. The apparent partition coefficient of contaminant in each sediment was estimated from predicted changes in pore-water and solid concentrations.

Boundary conditions for apparent partition coefficient estimation are

$$\begin{aligned} \frac{\partial C_W^A}{\partial x} &= 0 \quad \text{at } x = 0 \text{ for the amorphous organic matter} \\ \frac{\partial C_W^C}{\partial x} &= 0 \quad \text{at } x = 0 \text{ for the condensed-phase organic matter} \\ \frac{\partial C_W}{\partial t} &= -\frac{D_{\text{eff}}^A}{v_A} \cdot \frac{\partial C_W^A}{\partial x} \bigg|_{x=(V/A)^A} + \frac{D^C \cdot K_{OC}^C \cdot f_{oc/om}^C \cdot \rho^C}{v_C} \cdot \frac{\partial C_W^C}{\partial x} \bigg|_{x=(V/A)^C} \\ &\quad \text{at the interface of organic matter and} \\ &\quad \text{sediment pore water} \end{aligned} \quad (11)$$

where  $C_W$  is the aqueous concentration of contaminant,  $v_i$  ( $i = A$  or  $C$ ) is the ratio of water to organic matter by volume for the amorphous and condensed-phase organic matter, and

$$v_i = \left(\frac{W}{S}\right) \cdot \frac{\rho^i}{\rho_{\text{water}}} \cdot \frac{f_{oc/om}^i}{f_{oc}^i} \cdot \left(\frac{V}{A}\right)^i \quad (12)$$

where  $W/S$  is the mass ratio of water to sediment for the apparent partition coefficient estimation. This approach also could be used to simulate the influence of aging by extending time and considering  $W/S$  to be appropriate for the in situ water to sediment ratio.

#### Model parameters

The parameters used for the model are listed in Table 1. Properties of organic matter needed for the model include porosity,  $\varepsilon$ ,  $V/A$ , bulk density,  $\rho^A$ ,  $f_{oc/om}^A$ , and the total amorphous organic carbon content in sediment ( $f_{oc}^A$ ). Because the kinetics of desorption from the amorphous organic matter is very fast compared to that from the condensed-phase organic matter, pore-water concentrations and effective partition coefficients after 1 to 2 d are insensitive to rate-related parameters, such as  $\varepsilon$  and  $V/A$ . The value of  $\varepsilon$  was taken to be 0.4 and that of  $V/A$  20  $\mu\text{m}$ , although Wu and Gschwend [28] fitted their experimental data and reported the intra-aggregate porosity in sediment to be in a range of from 0.07 to 0.17. Arocha et al. [29] simulated intraparticle porosity to be 0.11 and 0.26 in a montmorillonite and a silt loam, respectively. The bulk density of the amorphous organic matter ( $\rho^A$ ) was chosen to be 1.5  $\text{g}/\text{cm}^3$ . Amorphous organic matter ( $f_{oc/om}^A$ ) was assumed to be 58% organic carbon using the typical ratio of 1:1.72 for organic carbon to organic matter [30].

The bulk density of the condensed-phase organic matter ( $\rho^C$ ) was chosen to be 1.8  $\text{g}/\text{cm}^3$ . Condensed-phase organic matter ( $f_{oc/om}^C$ ) was assumed to be 80% organic carbon based on the organic carbon content for coal-like particles in Utica Harbor sediment [27] and literature values [31]. The condensed-phase organic matter content was defined operationally by the remaining organic matter in sediment after the sediment had been heated at 375°C for 24 h [19]. Although this procedure for separating amorphous and condensed-phase organic carbon is commonly used [32–34], it is simply an operational definition [35]. The effective diffusion coefficient and  $V/A$  for the condensed-phase organic matter were obtained by fitting experimental data as described below.

Table 1. Key parameters used in the model

Symbol	Description	Source (value)
<b>Condensed organic matter properties</b>		
$\rho^C$	Density of the condensed-phase organic matter	1.8 g/cm <sup>3</sup>
$f_{oc/om}^C$	Fraction of organic carbon to organic matter for the condensed-phase organic matter	Measured on physically separated coal-like particles and Jonker and Koelmans [31] (0.80)
$f_{oc}^C$	Condensed-phase organic carbon content in sediment	Measured by technique of Gustafsson et al. [19]
$(V/A)^C$	Volume to surface area ratio for the condensed-phase organic matter	Fitted parameter
<b>Contaminant properties</b>		
$D$	Diffusivity of contaminant in pure water	U.S. Environmental Protection Agency [36]
$D^C$	Diffusivity of contaminant in condensed-phase organic matter	Fitted parameter
$K_{OC}^A$	Organic carbon-normalized partition coefficient for amorphous-phase organic matter	Mackay et al. [38]
$K_{OC}^C$	Organic carbon-normalized partition coefficient for condensed-phase organic matter	Measured on physically separated coal-cinder particles (5–10 $K_{OC}^A$ )

The diffusivity of various PAH contaminants in pure water ( $D$ ) was estimated from the U.S. Environmental Protection Agency [36]. The diffusivity in the amorphous organic matter was related to porosity by the model of Millington and Quirk [37]. The organic carbon-normalized partition coefficient of contaminant for the amorphous organic matter ( $K_{OC}^A$ ) was obtained from the literature, as calculated from the octanol-water partition coefficient by Mackay et al. [38] using the correlation by Karickhoff et al. [7]:  $\log K_{OC} = 1.0 \cdot \log K_{ow} - 0.21$ . The organic carbon-normalized partition coefficient of contaminant for the condensed-phase organic matter ( $K_{OC}^C$ ) was obtained from experimental measurement after 10 d of equilibration under conditions of neutral pH for coal-cinder particles separated from the field-contaminated sediment (Table 2) [27]. Although desorption generally is slow from the condensed phase, a period of 10 d was expected to be adequate for equilibration between water and the surface of the condensed-phase organic matter. The slow desorption and significant depletion of the condensed phase are not required for equilibration with a small volume of water. The differences between measured  $K_{OC}^C$  and literature  $K_{OC}$  values for other compounds were 0.7 to 1.2 logarithmic units. The only exception was that the measured  $K_{OC}^C$  for pyrene was only 0.28 log units greater than the literature  $K_{OC}$ . This anomalously low condensed-phase sorption coefficient (see, e.g., [31]) is not consistent with the large fraction of contaminant mass sorbed into the condensed-phase carbon, and the  $K_{OC}^C$  for pyrene was adjusted to 0.7 logarithmic units greater than the literature  $K_{OC}$ . This adjustment does not significantly influence short-term sorption and desorption, but it does affect the proportion of mass in the amorphous and condensed phases during long-term sorption simulations and,

thus, the potentially available fast-release fraction in field-contaminated sediments.

The condensed-phase organic matter diffusivity ( $D^C$ ) and effective  $V/A$  ( $(V/A)^C$ ) were fitted to measured pore-water concentrations, partition coefficients, and fast-release fractions collected for the four PAHs on the two sediments. The procedures for the measurements of the fitting data have been described elsewhere [27] but are summarized below.

Pore-water concentrations and partition coefficients were measured with 2 g of wet sediment (moisture content, ~40% wet wt) with known initial contaminant concentration. A 50-ml amber glass bottle with a Teflon®-lined screw cap was then filled with electrolyte solution (0.01 M NaCl, 0.01 M CaCl<sub>2</sub>·2H<sub>2</sub>O, and 0.01 M NaN<sub>3</sub> in deionized water) with minimal headspace. At the end of the equilibration time of 10 d, the sediment slurry was centrifuged (2,000 g, 20 min). Aqueous samples were then taken from each bottle, and the contaminant concentration in the aqueous phase was analyzed by high-performance liquid chromatography.

The fast-release fraction was measured by the fraction of contaminant removed by mixing sediments with Amberlite XAD-2 (Supelco, Bellefonte, PA, USA), a nonpolar polymer resin sorbent. Addition of such a sorbent has been used as an indicator of the fast-desorbing fraction or of bioavailability [27,39–41]. From 100 to 200 g of wet sediment (moisture content, 40–50% wet wt) were placed in a glass jar and mixed homogeneously with 10% (dry mass ratio) XAD-2. After 20 h of contact time, the XAD-2 was separated by addition of 100 ml of a cesium chloride solution, with a density of 1.1 g/ml to 20 g of sediment/XAD-2 mixture. The mixture was then allowed to settle for 10 to 15 min, until the XAD-2 floating

Table 2. Parameters used for modeling desorption and partitioning of polycyclic aromatic hydrocarbons from Utica Harbor (Utica, NY, USA) and Rouge River (Detroit, MI, USA) sediments<sup>a</sup>

Compound	Log $K_{OC}^A$	Log $K_{OC}^C$	$D$ (m <sup>2</sup> /s)	$D^C$ (m <sup>2</sup> /s)	$(V/A)^C$ (μm)
Phenanthrene	4.36	5.10	7.74E-10	8.50E-20	2
Anthracene	4.33	5.07	7.74E-10	8.50E-20	2
Pyrene	4.97	5.60	7.24E-10	8.50E-20	2
Benzo[a]pyrene	5.83	6.86	5.80E-10	8.50E-20	2

<sup>a</sup> Log  $K_{OC}^A$  is the literature partition coefficient [7, 38]; log  $K_{OC}^C$  is measured according to procedures described by Chai et al. [27] for coal-cinder particles isolated from Utica Harbor sediment except for pyrene, which was adjusted from 5.25 to 5.60 for consistency. Aqueous diffusivity ( $D$ ) was obtained according to U.S. Environmental Protection Agency [36];  $D^C$  and  $(V/A)^C$  are best-fit values. See Table 1 for definitions of parameters.



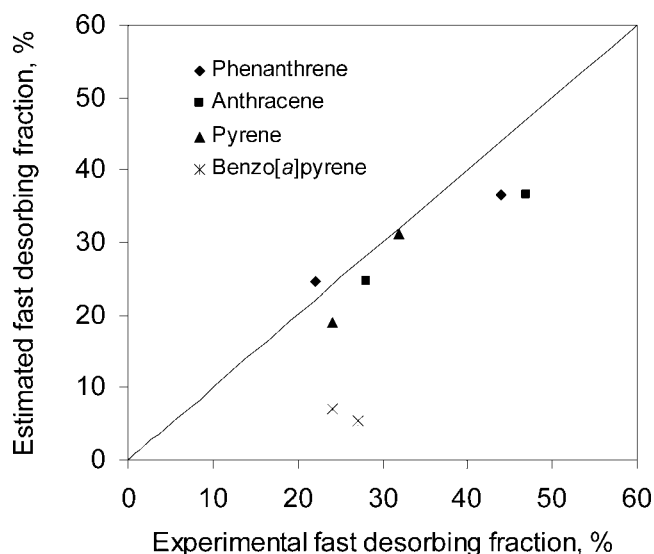


Fig. 1. Experimental results and model prediction for the fast-desorbing fraction of PAHs in Utica Harbor (Utica, NY, USA) and Rouge River (Detroit, MI, USA) sediment.

on the surface could be clearly separated from the sediment suspension. The sediment was separated from the cesium chloride solution by centrifugation (2,000 g, 20 min) and washed with tap water three times to remove any residual salt. Sediment was then collected to measure chemical concentrations and moisture content in triplicates. The condensed-phase organic matter diffusivity ( $D^c$ ) and  $(V/A)^c$  were fitted by minimizing the sum of squared differences between model simulations and measurements of partitioning and the fast-release fraction as measured by sorption with XAD-2. Model simulations included sorption for a long period (50 years) of sorption and desorption.

## RESULTS AND DISCUSSION

The fitted parameters are listed in Table 2 along with the corresponding measured parameters, including the amorphous diffusivities and the amorphous and condensed-phase partition coefficients. The value of  $(V/A)^c$  should be a function of the sediment and not compound specific. The condensed-phase diffusivity would be expected to have only a weak dependence on compound in this homologous series of contaminants, and this compound dependence was neglected. The fitted diffusivity of PAHs in condensed-phase organic matter was  $8.5 \times 10^{-20}$  m<sup>2</sup>/s, and the  $V/A$  was  $2 \times 10^{-6}$  m. The same set of parameters was applied to all PAHs and both Utica Harbor and Rouge River sediments even though the sediments exhibit significant differences in total organic carbon contents and the amorphous and condensed-phase organic carbon contents.

These parameters estimated measured pore-water concentrations of all PAHs in both sediments with an average relative error ((observed – predicted)/observed) of 46% and  $r^2$  of 0.76 and the fast-desorbing fractions with an average relative error of approximately 30% and  $r^2$  of 0.54. The prediction of pore-water concentrations was not significantly better or worse for any particular compound or sediment.

The fast-desorbing fraction of contaminants has been used as a surrogate indicator of availability [27,39–41], and model estimates of the fast-desorbing fraction showed generally good agreement between model and measurement, with the greatest errors being associated with benzo[a]pyrene (Fig. 1). The model does not include the effect of partitioning of colloidal organic matter between sediment and water on the rate of desorption, however, and this effect would have the greatest influence on the hydrophobic benzo[a]pyrene. With the exception of benzo[a]pyrene, the model predicted the fast-desorbing fraction with an average relative error of 14% and  $r^2$  of 0.76. The error associated with benzo[a]pyrene also may be associated with the larger molecular size of the compound, influencing both diffusion coefficients (as indicated above), or to the steric hindrance to diffusion of the compound in the organic matter. All simulations also are dependent on the assumption of constant concentration during the long period of sorption, because the most significant factor defining the fast-release fraction is the mass that had sorbed onto the amorphous and condensed phases. Thus, the model test evaluated in Figure 1 is more sensitive to the assumptions of the sorption simulation than to desorption.

The extremely small diffusivities of PAHs in the condensed-phase organic matter as estimated in the present study were comparable to other reported diffusivities of hydrophobic organic contaminants in condensed-phase organic matter. Ghosh et al. [20] estimated PAH diffusivities in coal-derived particles to be in the range of  $10^{-21}$  to  $10^{-23}$  m<sup>2</sup>/s. Carroll et al. [42] calculated an effective diffusivity for polychlorinated biphenyls in the range of  $10^{-24}$  to  $10^{-25}$  m<sup>2</sup>/s in polymeric soil organic matter. The fitted condensed-phase diffusivity also was very small compared to water or amorphous carbon diffusivity estimates but was larger by one to five orders of magnitude than these reported estimates.

### Sensitivity to fitted parameters

A sensitivity analysis was conducted by varying the fitted parameters,  $D^c$ , and  $V/A^c$ , in the condensed-phase organic matter. The relative error and correlation coefficient for the model-estimated pore-water concentration and apparent partition coefficient in Utica Harbor and Rouge River sediments are shown in Table 3 for various values of these parameters. The relative error and correlation coefficient for the model-estimated, fast-desorbing fractions in Utica Harbor and Rouge River sedi-

Table 3. The average relative error (Err) and correlation coefficient ( $r^2$ ) for model-estimated pore-water concentration and apparent partition coefficient in Utica Harbor (Utica, NY, USA) and Rouge River (Detroit, MI, USA) sediments<sup>a</sup>

Scenario	$D^c$ (m <sup>2</sup> /s)	$(V/A)^c$ (μm)	Average Err for $C_w$	$r^2$ for $C_w$	Average Err for log $K_{oc}$	$r^2$ for log $K_{oc}$
1	$8.5 \times 10^{-20}$	2	46.55	0.76	3.49	0.92
2	$8.5 \times 10^{-19}$	20	50.39	0.69	7.30	0.68
3	$8.5 \times 10^{-20}$	20	84.98	0.51	6.27	0.80
4	$8.5 \times 10^{-21}$	20	346.2	0.42	10.57	0.72
5	$8.5 \times 10^{-20}$	200	568.2	0.38	13.77	0.65

<sup>a</sup> See Table 1 for definitions of parameters. Average relative error was calculated as (observed – predicted)/observed·100%.

Table 4. The average relative error (Err) and correlation coefficient ( $r^2$ ) for model-estimated fast-desorbing fraction in (Utica, NY, USA) and Rouge River (Detroit, MI, USA) sediments<sup>a</sup>

Scenario	$D^c$ (m <sup>2</sup> /s)	(V/A) <sup>c</sup> (μm)	Average err (with BaP) (%)	$r^2$ (with BaP)	Average err (without BaP) (%)	$r^2$ (without BaP)
1	$8.5 \times 10^{-20}$	2	29.65	0.54	14.45	0.76
2	$8.5 \times 10^{-19}$	20	33.95	0.53	17.61	0.70
3	$8.5 \times 10^{-20}$	20	28.21	0.45	11.39	0.86
4	$8.5 \times 10^{-21}$	20	79.58	0.36	87.4	0.52
5	$8.5 \times 10^{-20}$	200	122.3	0.40	152.2	0.50

<sup>a</sup> See Table 1 for definitions of parameters. Average relative error was calculated as (observed – predicted)/observed·100%. BaP = benzo[a]pyrene.

ments are shown in Table 4. The results were relatively insensitive to parameter values, with changes in diffusivity ( $D^c$ ) of an order of magnitude or more being required to affect the correlation between the model and observations significantly. The model could be fitted to a particular compound and a particular sediment with less error, but that would defeat the purpose of the model (i.e., to predict with reasonable accuracy the pore-water concentrations and apparent partition coefficients on the basis of readily measurable or estimated parameters).

Because the estimations of the fast-release fraction for the two sediments and the four PAH compounds involved simulation of a long period of sorption, the most sensitive parameters are the partition coefficients,  $K_{OC}^A$  and  $K_{OC}^C$ , because these quantities largely define the ratio of the contaminant sorbed to the amorphous and condensed-phase carbon at the end of the sorption phase. In the absence of direct measurements of the quantity sorbed into these phases or measurements of these partition coefficients, literature estimates are available if the organic carbon in the sediments has been characterized (see, e.g., [31]).

#### Model-predicted sorption and desorption behavior

The model was employed to illustrate the sorption and desorption behavior of contaminants in a sediment containing both amorphous and condensed-phase organic matter. The modeling of phenanthrene in a model sediment with an organic carbon content of 2% (90% amorphous and 10% condensed phase) was used to demonstrate the character of the model predictions. The modeling results for other processes in this section, including desorption, aging, and apparent partitioning and desorption isotherms, were obtained based on this model sediment as well.

During sorption processes, the contaminant concentration in the solid phase increases rapidly at first because of sorption onto the amorphous organic matter and then very slowly because of sorption onto the condensed-phase organic matter. As a result of the slow uptake kinetics in the condensed phase, the bulk sediment loading and the effective partition coefficient would appear to be essentially independent of time after 24 h. Normal experimental uncertainty would require uptake for long periods (weeks or months) to detect changes in the effective partition coefficient resulting from slow sorption onto the condensed-phase organic matter.

During desorption, the amorphous organic matter rapidly achieves equilibrium, whereas the condensed-phase remains well away from equilibrium even after long periods of time. After short periods of time, the desorption is controlled by the condensed-phase organic carbon; thus, some hysteresis in the measured partition coefficient typically is noted between sorption and desorption experiments of equal duration, as noted

by Kan et al. [21]. The difference between sorption- and desorption-measured partition coefficients would decrease as desorption time increases. Similarly, the difference between partition coefficients measured in fixed-duration desorption experiments would increase with time of sorption or aging.

The effect of this aging phenomena was modeled by simulating continued diffusion during storage (in this case, for 1,000 d) after inoculation. Boundary conditions were the same as those for the estimation of the apparent partition coefficient described above. During storage, however, a very small water to solid ratio was employed to simulate the wet sediment. The water to solid ratio for the wet sediment was 0.67 to 1 g/g. The initial condition for the aging process was the endpoint of the sorption process. Model demonstration of pore-water concentration in amorphous organic matter and the virtual equivalent pore-water concentration in condensed-phase organic matter at different times during aging for the model sediment is shown in Figure 2. The contaminant migrates from the amorphous organic matter into the condensed-phase organic matter at a very slow rate during the aging process. Ultimately, both the amorphous and condensed-phase organic carbon achieve equilibrium with the pore-water concentration. This process would require many years, however, depending on the quantity of condensed-phase organic carbon.

Desorption kinetics were obtained after the aging process, assuming a boundary condition of zero concentration in the sediment pore water and simulating phenanthrene desorption. Figure 3 shows modeled results for desorption kinetics immediately after inoculation and after aging for 1,000 d. As the

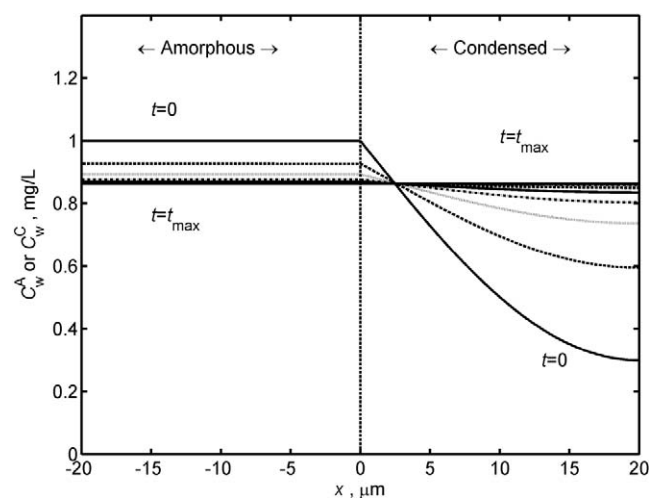


Fig. 2. Pore-water concentration profile during the aging process showing redistribution of a portion of the contaminant sorbed onto amorphous carbon into condensed-phase carbon, ultimately ( $\gg 1,000$  d) achieving a constant pore-water concentration.

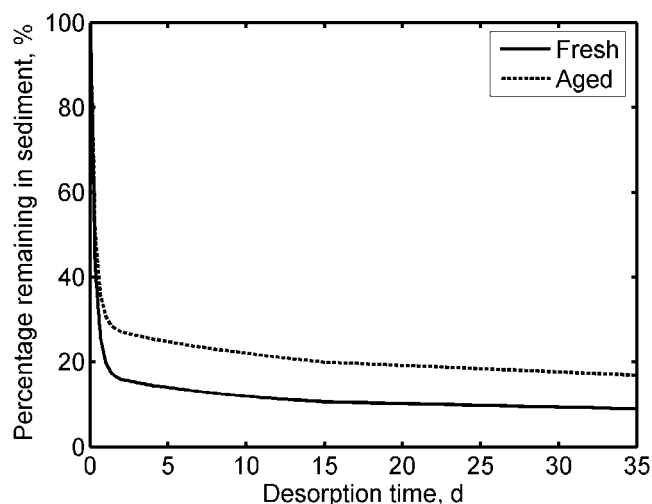


Fig. 3. Model-predicted desorption kinetics of phenanthrene from freshly inoculated and aged (for 1,000 d) model sediment.

aging time increases, a larger fraction of slow-desorbing contaminant is observed, increasing the mass retained on the solid and the effective partition coefficient and decreasing the pore-water concentration at any given time. Figure 4 shows modeled desorption isotherms for the freshly inoculated and aged (for 1,000 d) model sediment. Aging increased the mass of phenanthrene resistant to desorption, and this was reflected by an apparent increase in partition coefficient, as indicated by an increased sediment loading for a given pore-water concentration. For the model sediment, this increased partition coefficient was most apparent between 0.02 and 0.2 mg/L of phenanthrene, and the partition coefficient increase was approximately a factor of two over the 1,000 d of aging. These model results are consistent with the qualitative behavior of aging and sorption/desorption from contaminated sediments [21].

### CONCLUSIONS

In summary, the model was observed to provide semi-quantitative predictions of the kinetics and extent of desorption of four PAHs from two field-contaminated sediments. The ability to describe, approximately, behavior such as the fast-release contaminant fraction, pore-water concentrations, and effective

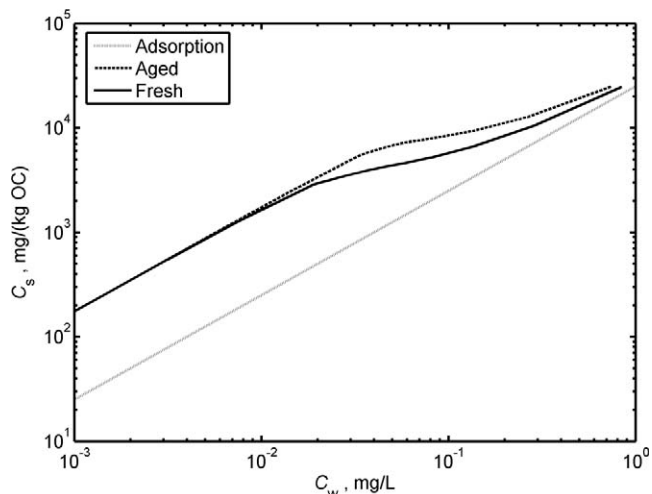


Fig. 4. Model-predicted desorption isotherms of phenanthrene in freshly inoculated and aged (for 1,000 d) model sediment.

partition coefficients based on independently measurable quantities and a single set of fitting parameters associated with the condensed-phase carbon was unexpected. The qualitative behavior of simulations on a hypothetical sediment also were consistent with observations that have been reported previously. The authors hope to be able to extend the range of contaminants and sediments that can be used to test or further develop the model. Ultimately, the authors hope that such a model can provide a quantitative tool for predicting pore-water concentration as an indicator for the bioavailability of hydrophobic organic contaminants in sediments.

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